

AD-A079 882

DEFENCE RESEARCH ESTABLISHMENT SUFFIELD RALSTON (ALBERTA) F/6 7/4
A CHROMATOGRAPH INJECTION VALVE - AN APPARATUS FOR RAPID INSERT--ETC(U)
DEC 79 W J FENRICK, W C CARPENTER
DRES-TN-402

UNCLASSIFIED

NL

[X]

ALL INFORMATION CONTAINED HEREIN IS UNCLASSIFIED



END

DATE

FEB 80

2 - 80

BY

UNCLASSIFIED

UNLIMITED
DISTRIBUTION

1-3
DRES

LEVEL II

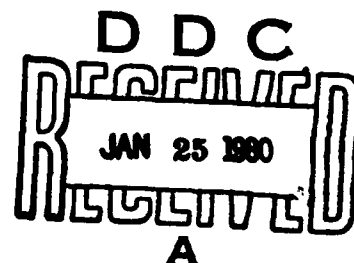
SUFFIELD TECHNICAL NOTE

NO. 402

A CHROMATOGRAPH INJECTION VALVE -
AN APPARATUS FOR RAPID INSERTION OF MINIATURE GLASS SAMPLERS
INTO THE CARRIER GAS FLOW OF A GAS CHROMATOGRAPH (U)

by

W.J. Fenrick and W.C. Carpenter



Project No. 13E01

December 1979

DDC FILE COPY



DEFENCE RESEARCH ESTABLISHMENT SUFFIELD : RALSTON : ALBERTA

WARNING

The use of this information is permitted subject to recognition
of proprietary and patent rights.

80 1 25 052

(14) DRES-TN-402

UNCLASSIFIED

UNLIMITED
DISTRIBUTION

DEFENCE RESEARCH ESTABLISHMENT SUFFIELD
RALSTON ALBERTA

(9) SUFFIELD TECHNICAL NOTE NO. 402

(6) A CHROMATOGRAPH INJECTION VALVE -
AN APPARATUS FOR RAPID INSERTION OF MINIATURE GLASS SAMPLERS
INTO THE CARRIER GAS FLOW OF A GAS CHROMATOGRAPH.

by

(10) W.J. Fenrick ~~and~~ W.C. Carpenter

Project No. 13E01

(11) Dec 79

(12) 20

WARNING
The use of this information is permitted subject to recognition
of proprietary and patent rights.

UNCLASSIFIED

403104 Jw A

Accession For	
NTIS GRA&I <input checked="" type="checkbox"/>	
DDC TAB <input type="checkbox"/>	
Unannounced Justification <input type="checkbox"/>	
By _____	
Distribution/ _____	
Availability Codes	
Dist	Avail and/or special

UNCLASSIFIED

DEFENCE RESEARCH ESTABLISHMENT SUFFIELD
RALSTON ALBERTA

SUFFIELD TECHNICAL NOTE NO. 402

A CHROMATOGRAPH INJECTION VALVE -
AN APPARATUS FOR RAPID INSERTION OF MINIATURE GLASS SAMPLERS
INTO THE CARRIER GAS FLOW OF A GAS CHROMATOGRAPH (U)

by

W.J. Fenrick and W.C. Carpenter

ABSTRACT

An injection valve for the rapid insertion of miniature glass samplers into the column of a gas chromatograph has been designed and tested. The valve is constructed so that the carrier gas can be allowed to bypass the injection system and flow directly into the column or it can be diverted through a glass sampler tube where it entrains desorbed vapours and carries them into the chromatograph column. Diversion of the carrier gas is so rapid that the operational stability of the gas chromatograph is not affected. A description and general assembly drawing of the unit, together with experimental evidence of its performance, are presented.

(U)

UNCLASSIFIED

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the valuable design contributions made by Mr. G.N. Schmitz. They also express their appreciation for the excellent craftsmanship, essential for the successful fabrication of the valve assembly, provided by Mr. D.J. Lonson. In addition they extend their gratitude to Mr. R.P. Hicken, Mr. C.E. Lough and Mr. L.R. Provost for the analytical data collection for this paper.

UNCLASSIFIED

DEFENCE RESEARCH ESTABLISHMENT SUFFIELD
RALSTON ALBERTA

SUFFIELD TECHNICAL NOTE NO. 402

A CHROMATOGRAPH INJECTION VALVE -
AN APPARATUS FOR RAPID INSERTION OF MINIATURE GLASS SAMPLERS
INTO THE CARRIER GAS FLOW OF A GAS CHROMATOGRAPH (U)

by

W.J. Fenrick and W.C. Carpenter

INTRODUCTION

For many years samples of atmospheric contaminants have been obtained by drawing the air through a glass tube packed with an adsorbent solid such as silica gel. Until recently the amount of contaminant has been determined by color reactions taking place within the sampler. In some cases the color is developed as the contaminant reacts with a coating on the adsorbent, while in others reagents are added to induce the color formation. With the advent of extremely sensitive liquid and gas chromatographic analytical methods it has become feasible to extract the adsorbed contaminant by various means for chromatographic analysis. Commonly the extraction is carried out by the use of solvents or by heating the sample in a gas stream and collecting

UNCLASSIFIED

the vapours in bubblers or cold traps. These methods are time consuming and subject to many sources of error. Frequently the result is a solution of the vapours, which is then introduced into the chromatograph. In the case of gas chromatographs, particularly, only a small percentage of the total solution can be used in an analysis, resulting in a corresponding loss of sensitivity.

If the sample could be totally desorbed directly into the inlet of the chromatograph the weaknesses of current systems would be largely overcome.

One type of the solid phase sampler is a 4 mm OD glass tube 40 mm in length. The central 20 mm holds the adsorbent which is kept in place by a suitable retainer, commonly cloth. A version of this sampler using specially shaped 600 mesh stainless steel screen to retain the packing will withstand the strong heating required to rapidly desorb the vapour loading. This "mini-tube" may be inserted into the sample inlet port of some gas chromatographs, where the sample is heated, desorbed and the vapours swept onto the column for analysis. However, to insert the mini-tube into the sample input port the port must be opened, resulting in loss of column pressure and interruption of column gas flow. This configuration is illustrated in Figure 1, which also shows that carrier gas may bypass the sampler by flowing around the outside of the tube. Disruption of the carrier gas flow affects the chromatograph operation to such an extent that in some cases the sample is lost before the operational stability of the column can be regained.

The chromatograph injection valve was designed to permit diversion of the carrier gas flow so that the mini-tube could be inserted with a minimum of column flow disruption, and to force the entire flow of carrier gas through the sampler. When the valve is in the bypass position (broken lines, Fig. 2), the sample chamber is isolated from the chromatograph column so that the chamber can be opened and the sampler inserted. As soon as the sample chamber has been resealed the valve rotor is rotated to the sample injection position (solid lines,

Fig. 2) and the desorbed sample is swept into the chromatograph column.

DESCRIPTION

A general assembly of the chromatograph sample injection valve is shown in Figure 3.

The valve operates as follows: the assembly is attached and sealed to the chromatograph sample port, No.1, by the adapter nut, No 2, and the septum, No. 3. The carrier gas supply line is coupled to the right angled Swagelok^{®1} fitting, No.4, which conducts the carrier gas to the inlet port of the valve body, No. 5. If the valve lever, No. 6, is pulled forward into the horizontal position, the passages in the valve rotor, No. 7, will assume the position designated by the broken lines. With the valve rotor in this position, carrier gas entering the valve flows directly into the chromatograph input port, No. 1, while the desorption chamber is left sealed and isolated from the carrier gas flow. Alignment of the passages in the valve body, No. 5, and the valve rotor, No. 7, in either of its positions, is maintained by specially designed stops machined on the valve body working in conjunction with a specially designed washer, No. 26, which together control the angular travel of the rotor.

To insert the mini-tube, No. 8, into the injection valve, the rotor, No. 7, is placed in the bypass position and the desorption chamber is decoupled at the multiple thread, No. 9. The sub-assembly, consisting of parts 10 to 17, is then removed and the mini-tube, No. 8, placed over the stainless steel tube, No. 11, so that it comes to rest against the Teflon^{®2} pad, No. 12. The sub-assembly is then quickly recoupled to the inner portion of the desorption chamber, No. 18, and securely tightened against the Teflon washer, No. 19. The mini-tube is

¹ Registered Trade Mark of Crawford Fittings (Canada) Ltd.

² Registered Trade Mark of E.I. Dupont de Nemours & Co.

thus held between the Teflon pad, No. 12, and the septum, No. 23, by the compression spring, No. 15.

The desorption chamber is maintained at a suitable temperature by the heat sink assembly, Nos. 20, 20A and 20B, which is heated by the thermostatically controlled heater, No. 21. Because the desorption chamber is maintained at an elevated temperature, desorption of the sample begins immediately upon insertion of the sampler. This is the reason the coupling thread, No. 9, is specified to be a multiple thread so that the coupling can be sealed as quickly as possible.

As soon as the mini-tube is sealed into the desorption chamber the adsorbent is heated and the vapours desorbed. The valve lever, No. 6, is moved quickly from the horizontal to the vertical position. The passages in the valve rotor, No. 7, are then aligned as is designated in Figure 3 by the solid lines, diverting the carrier gas through the desorption chamber with little or no disruption in the operational stability of the chromatograph column. The carrier gas enters the desorption chamber through a small hole drilled in the wall of the inner portion, travelling through the annular space between the inner wall of the desorption chamber and the outer surface of the mini-tube until it reaches the area where the compression spring, No. 15, is located. All of the carrier gas must then pass through the centre of the sample holder, No. 13, and enter the mini-tube through the stainless steel tube, No. 11. Because the carrier gas is prevented from escaping from the mini-tube by the Teflon pad, No. 12, and the septum, No. 23, it passes through the adsorbent and sweeps the desorbed sample through the stainless steel tube, No. 37, onto the chromatograph column.

The sample injection valve assembly is attached to the chromatograph at three points, one being the sample port, No. 1, with the other two being standoffs between the chromatograph and the mounting plate, No. 24. A photograph of the assembly mounted on the front of a chromatograph is shown in Figure 4.

The rotary valve and desorption chamber sub-assemblies are

fastened to the mounting plate, No. 24, by 4 binding head screws, No. 25, and are completely enclosed in the No. 20, 20A, 20B heat sink assembly, which it is necessary to produce in three pieces to permit complete enclosure over the valve rotor, No. 7, and the valve retaining components, Nos. 26 to 29. Two socket head cap screws, No. 30, are used to hold the two semicircular plates, Nos. 20A and 20B, in position while the main portion of the heat sink is held in place by a set screw, No. 31. The heat sink is covered with thermal insulation, No. 32, which is protected by the outer cover, No. 33.

The valve rotor, No. 7, is made of Vespel^{®3}, a polyimide resin developed by Dupont to operate without lubrication or appreciable out-gassing at elevated temperatures (260°C). In addition, Vespel is resistant to solvents and acids. All of these qualities contribute to the successful performance of the material for this particular application.

The design of the sample injection valve is such that "off-column" injections may be made without removing the valve from the chromatograph. The valve is assembled with a plain piece of glass tubing in the desorption chamber and the sample injected into the tubing, see Figure 4.

EXPERIMENTAL

The following experiment was conducted to evaluate the desorption and injection efficiency of the chromatograph sample injection valve.

Procedure

An adsorber of known and reliable characteristics (Tenax GC^{®4}) was used to collect samples of triethyl phosphate (TEP) vapour,

³ Registered Trade Mark of E.I. Dupont de Nemours & Co.

⁴ Registered Trade Mark of Enka N.V., The Netherlands.

which is also considered to be a material of known and reliable characteristics. The above combination of adsorber and adsorbate allows accurate prediction of the recovery data which should be indicated by the chromatograph and its associated data collection system.

Five injections each containing 10 nanograms of TEP in a suitable solvent were made through the valve and the areas under the resulting peaks determined.

After the standard injections were made the valve was set into the bypass position and the plain glass tube was removed.

Five mini-tube samplers, which have already been described, were used to collect TEP vapour samples from a controlled vapour source. Each mini-tube contained 10 nanograms of TEP.

In turn, each of the specially prepared mini-tubes was sealed into the desorption chamber, the valve switched to the sample injection position, the TEP vapours swept into the chromatograph and the areas under the resulting peaks determined.

Detector output was recorded on a strip chart recorder and also fed into a Peak-11 On-line Computer System. The peak area figures obtained from the computer as well as the GC parameters are shown in Table 1.

Conclusions

The data presented show that the injection valve system is capable of quantitatively transferring the contents of a sample contained in a mini-tube into a gas chromatograph for analysis, with a high degree of reproducibility.

APPLICATIONS

By making the appropriate changes in Parts Nos. 2 and 39 the valve may be adapted to fit a wide variety of instruments such as mass spectrometers and atomic absorption analyzers as well as most models of

gas chromatographs.

To date, many applications have been found whereby samples of contaminated air can be taken in the field using the mini-tubes and the samples subsequently analyzed in the laboratory using this injection valve assembly. The system works extremely well for many vapours.

The valve and glass sampler combination is also useful as a pre-column to protect the chromatograph column when liquid samples are analysed. If the liquid samples are contaminated by non-volatile contaminants they will collect in the chromatograph column packing, to the point where the column must be repacked or replaced. If such samples are injected into the packing in a glass sample tube mounted in the desorption chamber of the valve assembly as is shown in Figure 3, the residue will collect in the packing material within the glass tube. After several samples have been injected into the packing material within the glass tube and the concentration of residue has reached a significant level the tube can be discarded and replaced with a clean one. Alternately, if the substance being sought is not exceptionally volatile, specific volumes of each liquid sample can be injected into the packing of separate sample tubes, analyzed individually and disposed of.

PATENTS

The chromatograph sample injection valve described in this note has been patented in both Canada and the United States. Entitled "Chromatograph Injection System" by Carpenter, Wilfred C., Schmitz, Gary N. and Fenrick, Walter J., all of Defence Research Establishment Suffield, Canadian Patent No. 1055723 was issued 5 June 1979, U.S. Patent No. 4,084,440 on 18 April 1978. Both patents are vested in Her Majesty in Right of Canada in accordance with the Public Servants Invention Act.

UNCLASSIFIED

TABLE 1

EXPERIMENTAL DATA

Sample Number	Integrated Area Under Peak	
	Reference Samples	Mini-Tube Samples
1	790	820
2	830	840
3	820	860
4	840	860
5	890	860
Mean	834	848
S.D.	36	18

CHROMATOGRAPH PARAMETERS

Desorption Temperature - 210°C
Carrier - Nitrogen - 35 cc/min
Column - 1/8 in x 6 ft
Detector - Flame Photometric

UNCLASSIFIED

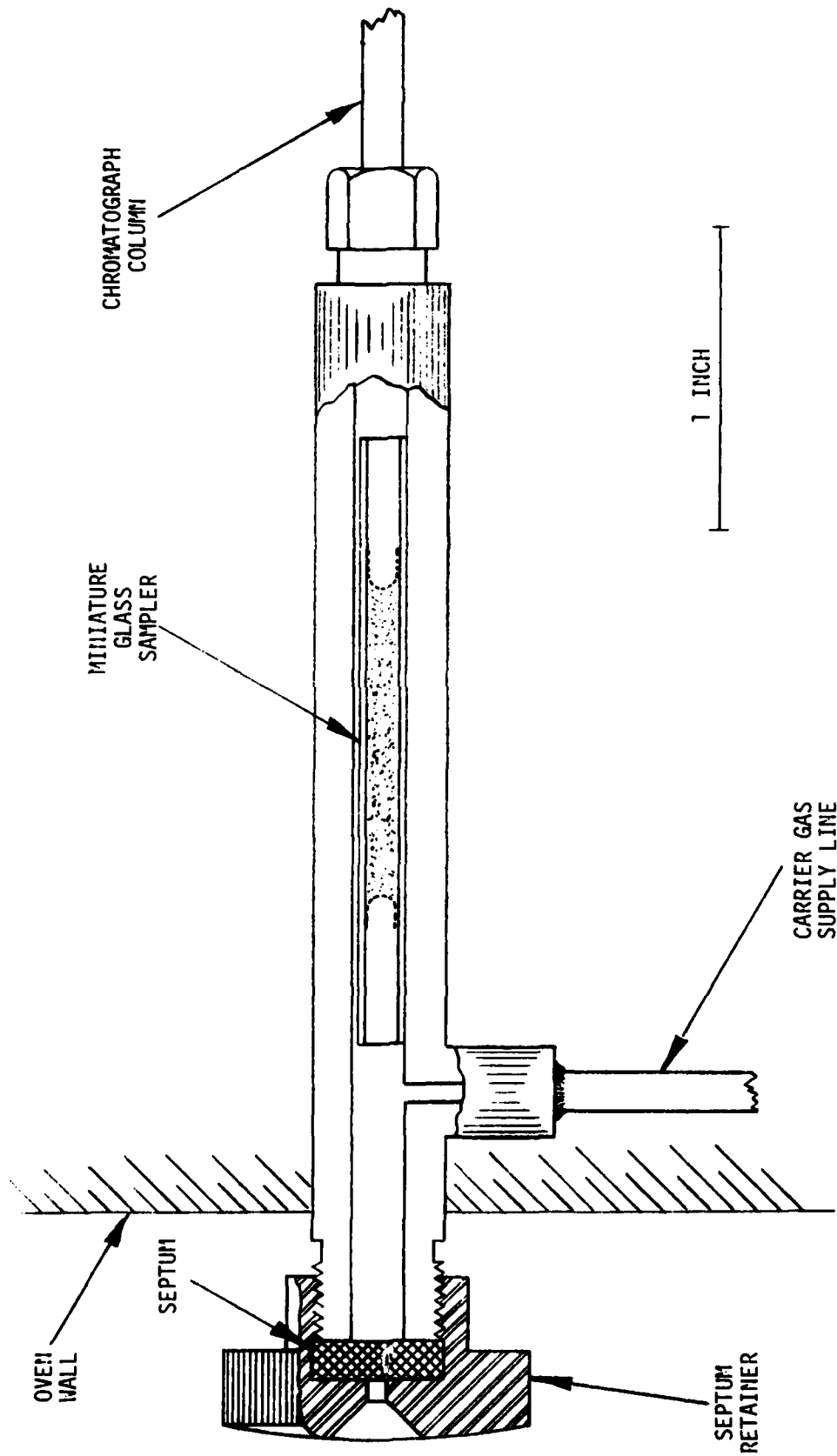
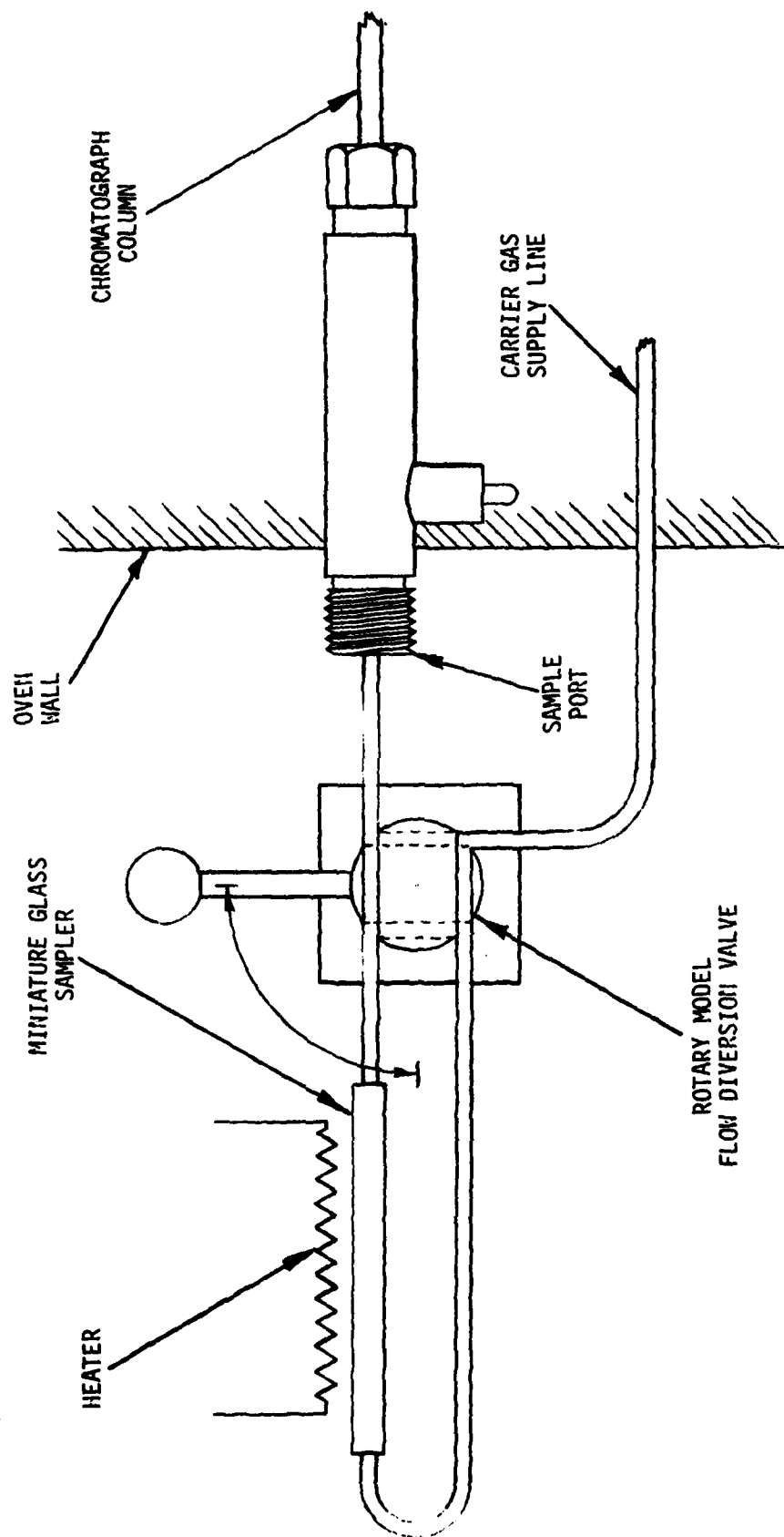


FIGURE 1 - MINIATURE GLASS SAMPLER AS INSERTED IN CHROMATOGRAPH SAMPLE PORT

UNCLASSIFIED

STN 402



UNCLASSIFIED

FIGURE 2 - SCHEMATIC DIAGRAM OF CHROMATOGRAPH SAMPLE INJECTION VALVE (ROTARY MODEL)

UNCLASSIFIED

PARTS LIST FOR SAMPLE INJECTION VALVE

1. Chromatograph Input Port
2. Chromatograph Adaptor Nut
3. Septum
4. Elbow 1/16" N.P.T. to 1/16" Swagelok
5. Valve Body
6. Valve Lever
7. Valve Rotor
8. Miniature Glass Sampler
9. Multiple Thread
10. "C" Ring
11. Stainless Steel Tube
12. Teflon Pad
13. Sample Holder
14. Outer Portion of Desorption Chamber
15. Compression Spring
16. Septum
17. Septum Retaining Cap
18. Inner Portion of Desorption Chamber
19. Teflon Washer
20. 20A and 20B Heat Sink Assembly
21. Cartridge Heater
22. Thermocouple
23. Septum

UNCLASSIFIED

UNCLASSIFIED

PARTS LIST FOR SAMPLE INJECTION VALVE (Cont'd)

- 24. Mounting Plate
- 25. Binding Head Machine Screws (4 x 40)
- 26. Angular Travel Limiting Washer
- 27. Compression Spring
- 28. Washer
- 29. Roll Pin
- 30. Socket Head Cap Screw
- 31. Allen Screw
- 32. Thermal Insulation
- 33. Outer Cover
- 34. Binding Head Machine Screw (4 x 40)
- 35. Threaded Insert
- 36. Stainless Steel Tube
- 37. Stainless Steel Tube
- 38. Teflon Ring 0.625" OD x 0.569" ID x 0.065 Thick
- 39. Chromatograph Inlet Adaptor

UNCLASSIFIED

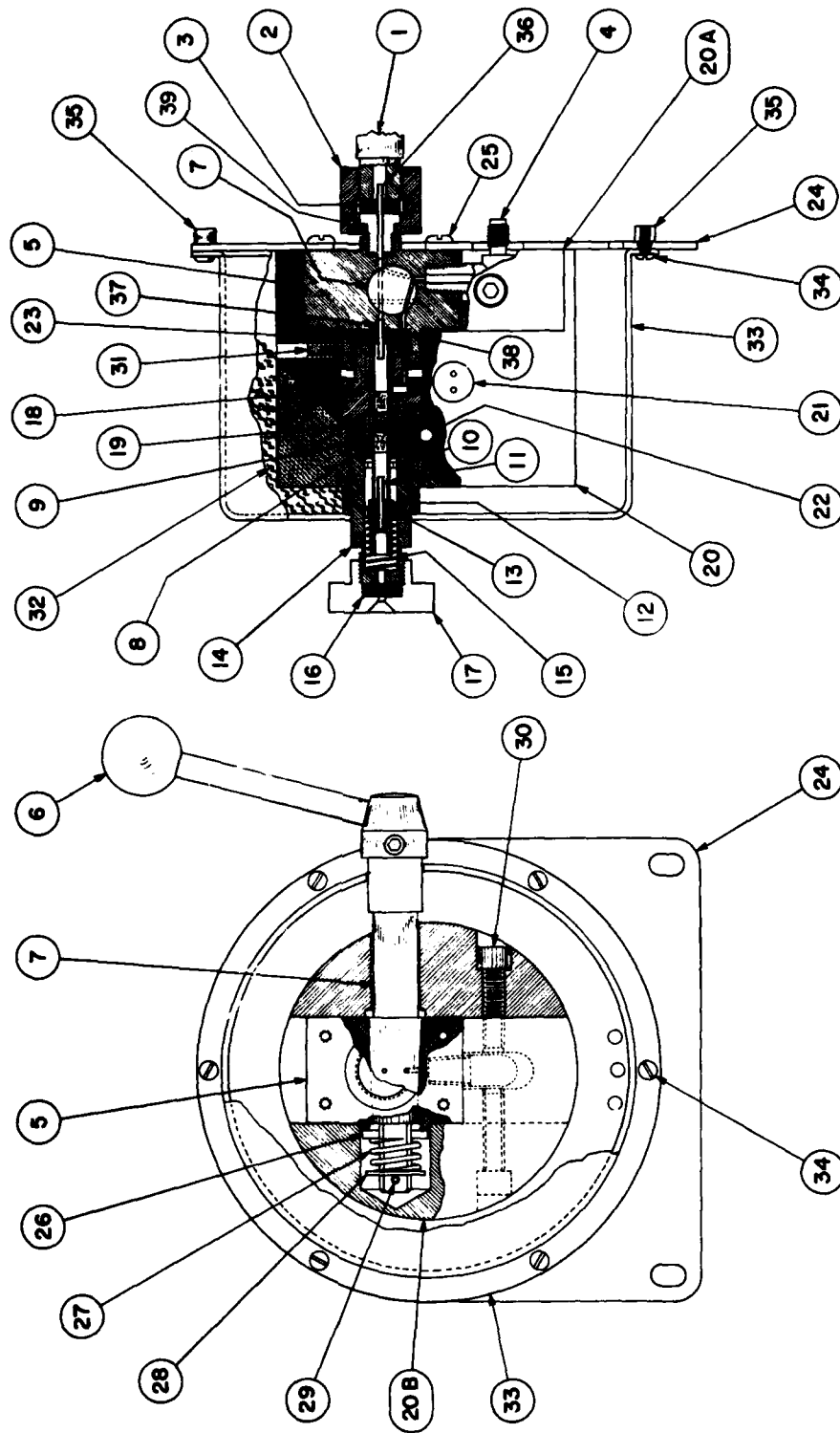


FIG. NO. 3 CHROMATOGRAPH SAMPLE INJECTION VALVE (ASSEMBLY)

UNCLASSIFIED

STN 402

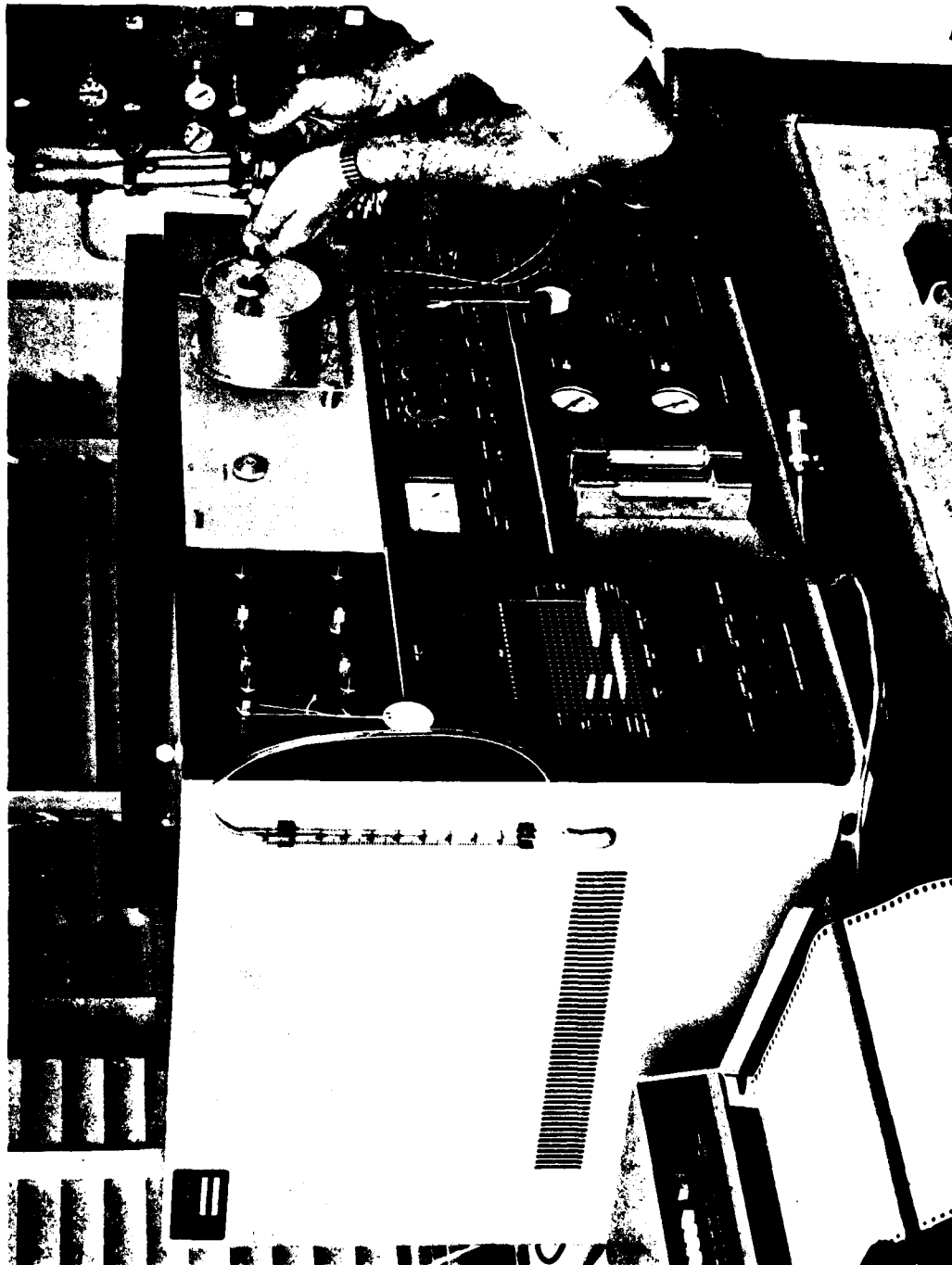


FIGURE 4 - INJECTION OF SAMPLE ONTO COLUMN THROUGH INJECTION VALVE

UNCLASSIFIED

UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall document is classified)

1. ORIGINATING ACTIVITY DEFENCE RESEARCH ESTABLISHMENT SUFFIELD ✓		2a. DOCUMENT SECURITY CLASSIFICATION UNCLASSIFIED	
		2b. GROUP	
3. DOCUMENT TITLE A CHROMATOGRAPH INJECTION VALVE - AN APPARATUS FOR RAPID INSERTION OF MINIATURE GLASS SAMPLERS INTO THE CARRIER GAS FLOW OF A GAS CHROMATOGRAPH (U)			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Technical Note			
5. AUTHOR(S) (Last name, first name, middle initial) Fenrick, W.J. and Carpenter, W.C.			
6. DOCUMENT DATE DECEMBER 1979		7a. TOTAL NO. OF PAGES 16	7b. NO. OF REFS -
8a. PROJECT OR GRANT NO. 13E01		8a. ORIGINATOR'S DOCUMENT NUMBER(S) SUFFIELD TECHNICAL NOTE NO. 402 ✓	
8b. CONTRACT NO.		8b. OTHER DOCUMENT NO.(S) (Any other numbers that may be assigned this document)	
10. DISTRIBUTION STATEMENT UNLIMITED DISTRIBUTION			
11. SUPPLEMENTARY NOTES		12. SPONSORING ACTIVITY	
13. ABSTRACT ↓ An injection valve for the rapid insertion of miniature glass samplers into the column of a gas chromatograph has been designed and tested. The valve is constructed so that the carrier gas can be allowed to bypass the injection system and flow directly into the column or it can be diverted through a glass sampler tube where it entrains desorbed vapours and carries them into the chromatograph column. Diversion of the carrier gas is so rapid that the operational stability of the gas chromatograph is not affected. A description and general assembly drawing of the unit, together with experimental evidence of its performance, are presented. ↖ (U)			

UNCLASSIFIED

Security Classification

KEY WORDS

Gas Chromatograph
Injection Valve
Sampling, gas

INSTRUCTIONS

1. **ORIGINATING ACTIVITY:** Enter the name and address of the organization issuing the document.
- 2a. **DOCUMENT SECURITY CLASSIFICATION:** Enter the overall security classification of the document including special warning terms whenever applicable.
- 2b. **GROUP:** Enter security reclassification group number. The three groups are defined in Appendix M of the DRS Security Regulations.
3. **DOCUMENT TITLE:** Enter the complete document title in all capital letters. Titles in all cases should be unclassified. If a sufficiently descriptive title cannot be selected without classification, show title classification with the usual one-capital-letter abbreviation in parentheses immediately following the title.
4. **DESCRIPTIVE NOTES:** Enter the category of document, e.g. technical report, technical note or technical letter. If appropriate, enter the type of document, e.g. interim, progress, summary, annual or final. Give the inclusive dates when a specific reporting period is covered.
5. **AUTHOR(S):** Enter the name(s) of author(s) as shown on or in the document. Enter last name, first name, middle initial. If military, show rank. The name of the principal author is an absolute minimum requirement.
6. **DOCUMENT DATE:** Enter the date (month, year) of Establishment approval for publication of the document.
- 7a. **TOTAL NUMBER OF PAGES:** The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.
- 7b. **NUMBER OF REFERENCES:** Enter the total number of references cited in the document.
- 8a. **PROJECT OR GRANT NUMBER:** If appropriate, enter the applicable research and development project or grant number under which the document was written.
- 8b. **CONTRACT NUMBER:** If appropriate, enter the applicable number under which the document was written.
- 9a. **ORIGINATOR'S DOCUMENT NUMBER(S):** Enter the official document number by which the document will be identified and controlled by the originating activity. This number must be unique to this document.
- 9b. **OTHER DOCUMENT NUMBER(S):** If the document has been assigned any other document numbers (either by the originator or by the sponsor), also enter this number(s).
10. **DISTRIBUTION STATEMENT:** Enter any limitations on further dissemination of the document, other than those imposed by security classification, using standard statements such as:
 - (1) "Qualified requesters may obtain copies of this document from their defence documentation center."
 - (2) "Announcement and dissemination of this document is not authorized without prior approval from originating activity."
11. **SUPPLEMENTARY NOTES:** Use for additional explanatory notes.
12. **SPONSORING ACTIVITY:** Enter the name of the departmental project office or laboratory sponsoring the research and development. Include address.
13. **ABSTRACT:** Enter an abstract giving a brief and factual summary of the document, even though it may also appear elsewhere in the body of the document itself. It is highly desirable that the abstract of classified documents be unclassified. Each paragraph of the abstract shall end with an indication of the security classification of the information in the paragraph (unless the document itself is unclassified) represented as (TS), (S), (C), (R), or (U).

The length of the abstract should be limited to 20 single-spaced standard typewritten lines; 7/8 inches long.
14. **KEY WORDS:** Key words are technically meaningful terms or short phrases that characterize a document and could be helpful in cataloging the document. Key words should be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context.